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Hierarchical nanoflowers assembled with Au nanoparticles decorated ZnO nanosheets toward enhanced photocatalytic properties

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ABSTRACT

Hierarchical nanoflowers assembled with Au nanoparticles (NPs) decorated ZnO nanosheets (Au-ZnO nanosheet flowers, AZNSFs) were successful synthesized. The AZNSFs showed more efficient activity to photodegradation of RhB than that of pure ZnO nanosheet flowers and commercial ZnO nanopowders. The improved photocatalytic properties of the AZNSFs nanohybrids are attributed to the large specific surface area induced by the 3D hierarchical architectures, stable structure and the charge separation due to the electronic interaction between Au NPs and ZnO nanosheets.

Keywords: Au-ZnO; Composite materials; Crystal growth; hierarchical nanostructures; photocatalytic activity

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1. Introduction

Hierarchical micro-/nanoarchitectures can not only inherit the excellent properties of the constituted nanobuilding blocks but also show special and multiple functionalities arising from the interaction of the low-dimensional structures [1]. We have synthesized three-dimensional (3D) hierarchical architectures by using 2D nanomaterials as nanobuilding blocks [2, 3]. The architectures possess high specific surface area, which is beneficial for the mass transportation and the increasement of active sites. Combining 2D nanomaterials with lower dimensional structures to form 0D-2D or 1D-2D heterostructures is a versatile method to avoid the agglomeration and induce additional functions. Considerable efforts has been on the synthesis of Au NPs modified ZnO nanostructures in order to enhance physical/chemical properties, nevertheless, poisonous precursors, reducing agents, and multistep heat treatment are frequently involved [4-6]. In this work, we describe a simple solution phase reaction combined with electrochemical deposition method to synthesize hierarchical nanoflowers assembled with 0D Au NPs decorated 2D ZnO nanosheets (Au-ZnO nanosheet flowers, AZNSFs). The photocatalytic properties of the unique AZNSFs are investigated. The 3D architectures constructed by 0D/2D hybrid structure combining the large specific surface area, stability and catalytic activity, demonstrate the higher photocatalytic abilities than that of pure ZnO nanosheet flowers (ZNSFs) and commercial ZnO nanopowders.

2. Experimental

Synthesis of ZNSFs was carried out by a simple solution phase approach [7]. AZNSFs sample was then synthesized by employing electrochemical deposition method. The electrolyte was made of 100 mL aqueous solution containing 1 mM $HAuCl_4 \cdot 4H_2O$. The deposition was performed at room temperature for 10 min by applying a voltage of 1 V and a current density of ~0.4 $mAcm^{-2}$. The samples were examined on a Bruker Model

D8 Advance X-ray powder diffractometer with Cu Kα irradiation, scanning electron microscopy (SEM, Hitachi-S5500, 5 kV), and transmission electron microscopy (TEM, JEM-2010F, 200 kV). The photocatalytic properties were investigated by the degradation of Rhodamine B (RhB, 1.0×10^{-5} M) under the illumination of ultraviolet (UV) irradiation at room temperature. After initiation of the reaction by irradiation, a sample (5 mL) of the suspension was taken out at regular intervals (~ 20 min) and centrifuged to completely remove the catalyst. In order to measure the RhB degradation, UV-visible spectra of the centrifuged solution was recorded by using UV-2550 UV-visible spectrophotometer (Shimadzu, Japan).

3. Results and discussion

Fig. 1a is a low-magnification SEM image of ZNSFs. It can be seen that the sample is assembled by 2D thin sheets to form a flower-like morphology. The surface of the sheets is flat and smooth, and the average thickness of the sheets is ~20 nm by analyzing the sheets vertical on the substrate. TEM and HRTEM results further confirms that the constituted building blocks of ZnO 3D hierarchical structures are 2D single crystal sheets (Fig. S1). Typical SEM image for AZNSFs sample (Fig. 1b) shows that the original flower-like morphology is preserved through the additional electrochemical deposition process. A close view of the composite nanostructure exhibits the distribution of Au NPs on the surface of each ZnO nanosheets (Fig. 1c), and it is interesting to find that Au NPs prefer to deposit on the edge of the single crystal nanosheets, which may attribute to the high active of the edge sites. The chemical composition of the product was analyzed by EDS, which indicates that the AZNSFs sample consists of Zn, O, Au elements, and the average atomic ratio of Au/Zn is ~0.04 (Fig.1d). Fig. 1e shows a typical TEM image of Au NPs decorated ZnO nansosheet. It can be clearly seen that Au NPs with an average size of 11 nm are uniformly distributed on the surface and edge of the ZnO nanosheet. Some Au NPs are agglomerated by smaller particles with the size ranged from 4 nm to 20 nm (Fig. S2). HRTEM image (Fig. 1f) shows the lattice fringes with spacing of ~2.59 and 2.32 Å, which can be assigned to the spacing of the (002) plane of ZnO (JCPDS

number: 36-1451) and (111) plane of Au (JCPDS number: 01-1172), respectively. Fig. 1g shows that Zn and O elements both have a uniform distribution throughout the whole sheet, while the Au element existed in the form of particle is distributed on the nanosheet. The successful deposition of Au NPs is also confirmed by the XRD patterns (Fig. S3 and 4).

Fig. 2a shows the chemical states of the Zn(II) species in AZNSFs composites as measured by X-ray photoelectron spectroscopy (XPS, Escalab 250, Al Ka). Two peaks centered at 1022.1 and 1045.2 eV are matching with the spin-orbit split of Zn $2p_{3/2}$ and Zn $2p_{1/2}$. The energy difference between these two peaks is 23.1 eV, which agrees well with the standard value of 22.97 eV [8]. Deconvolution of the O 1s peaks of the composites show three different kinds of oxygen related bonds (Fig. 2b), with peaks located at 532.8, 531.6 and 530.7 eV, which can be assigned to molecular water adsorbed on the surface, the OH^- group, and lattice oxygen, respectively [9]. The high resolution XPS spectrum shown in Fig. 2c was fitted to four peaks. The two peaks centered at 83.6 eV and 87.4 eV can be attributed to Au $4f_{7/2}$ and Au $4f_{5/2}$, respectively. The values suggest unambiguously that gold is only present in the metallic form, indicating the formation of Au NPs on the ZnO structure. The binding energy of Au $4f_{7/2}$ exhibits a negative shift of 0.2 eV in comparison to 83.8 eV of bulk Au. It is generally believed that the slight shift is caused by electron transfer from plasmonic Au NP to ZnO nanosheets due to the strong electronic interaction between the Au and oxide support, which has also been reported before [8, 10]. The Au $4f_{5/2}$ range overlaps with the Zn $3p_{3/2}$ and the Zn $3p_{1/2}$ peak contributions, and these peaks can be deconvoluted into two peaks: Zn 3p3/2 located at 89.2 eV and Zn3p1/2 located at 91.4 eV. The isotherm of the AZNSFs shows a wide hysteresis loop at relative pressure range of 0.45-1.0 P/P_0 and the corresponding specific surface area is ~ 40.2 m^2g^{-1}, which is larger than that of ZNSFs (~27.5 m^2g^{-1}) (Fig. S5a). In addition, the mesopore size distributions of AZNSFs and ZNSFs are further confirmed by the corresponding pore size distribution curves (Fig. S5b). The mesoporous structures can provide extra active sites for the diffusion and mass transportation of dye molecules and hydroxyl radicals, which

is important for photochemical reactions.

Fig. 3a shows UV-vis absorption spectra of the aqueous solution of RhB with a 20 mg of AZNSFs as the photocatalyst exposed to UV light for different time. The characteristic absorption of RhB centered at 552 nm decreases rapidly for AZNSFs photocatalyst with extending the exposure time, and completely disappears after 100 min. Fig. 3b shows the comparison of the time profiles of the decrease in RhB concentration in the absence and in the presence of different photocatalysts. The blank experiment (grey curve) with the absence of photocatalyst shows almost no degradation of RhB in UV light. Pure ZNSFs and commercial ZnO nanopowders (*c*-ZnO) show observable but rather sluggish photocatalytic activity under UV irradiation, removing ~65.4% and 61% of RhB from solutions after an illumination time of 100 min. In contrast, a significant synergistic enhancement effect of the photocatalyst is observed when the AZNSFs sample is applied as a photocatalyst. RhB dye is decomposed thoroughly within 90 min in the presence of the AZNSFs, demonstrating that the presence of Au NPs induces significant enhancement in the photodegradation efficiency (see also Table S1). Kinetics analysis (Fig. S6) and stability test (Fig. S7) further show that the AZNSFs sample is a very efficient and stable photocatalyst and the efficiency does not significantly decrease for the first three cycles of operation.

There are several reasons that are responsible for the enhanced photocatalytic activity of the AZNSFs. (1) The large surface area and interspaces in the Au NPs decorated ZNSFs offered more opportunity for the diffusion and mass transportation of RhB molecules and hydroxyl radicals in photochemical reaction of RhB degradation. (2) The strong electronic interaction between plasmonic Au NPs and ZnO nanosheets induces the charge transfer from ZnO to Au NPs and increase the efficiency of charge separation of the photo-generated electron-hole pairs [10]. (3) The Au-ZnO interfaces can lead to a substantial decrease in work function [11]. It will result in a significant increase in the rate of electron transfer to O_2, to yield highly active oxidizing species, which would substantially enhance the rate of photocatalytic reaction [12].

4. Conclusions

AZNSFs 3D architectures constructed by 0D/2D hybrids have been successfully synthesized by a facile solution phase reaction combined with electrochemical deposition method. The photodegradation of RhB by AZNSFs is more efficient than that of pure ZNSFs and commercial ZnO nanopowders. The current synthetic strategy can also be applied to yield other hybrid nanostructures with novel properties.

Acknowledgments

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Fig. 1 SEM images of (a) pure ZNSFs and (b, c) AZNSFs, (d) EDS spectrum of AZNSFs, (e) TEM and (f) HRTEM images of AZNSFs, (g) Elemental maps of Zn, O and Au for an individual nanosheet.

Fig. 2 High resolution XPS spectra of (a) Zn 2p, (b) O 1s and (c) Au 4f of AZNSFs.

Fig. 3 (a) Time dependent UV-vis spectral of RhB aqueous solution in the presence AZNSFs, (b) Photocatalytic degradation curves of RhB in the presence of different photocatalysts.